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(54) **Titre : CONCENTRES DE SUSPENSION A BASE D'HUILE**
(54) **Title: OIL-BASED SUSPENSION CONCENTRATES**

(57) **Abrégé/Abstract:**
There is provided an oil-suspension concentrate of an agrochemically active product, comprising: (A) imidacloprid; (B) at least one pyrethroid selected from the group consisting of beta-cyfluthrin and deltamethrin; (C) at least one penetrant; (D) at least one vegetable oil; (E) cyclohexanone; (F) at least one nonionic surfactant, at least one anionic surfactant or a mixture thereof; and (G) one or more additives selected from the group consisting of an emulsifier, a foam inhibitor, a preservative, an antioxidant, a spreader, a colorant, a thickener and a mixture thereof. A process for producing the oil-suspension concentrate comprises mixing (A) to (G) with one another and then grinding until an average particle size of less than 10 µm is reached. Also provided is a method of controlling harmful organisms by applying the oil-suspension concentrate to the insects or their habitats.

30725-1110

Abstract

There is provided an oil-suspension concentrate of an agrochemically active product, comprising: (A) imidacloprid; (B) at least one pyrethroid selected from the group consisting of beta-cyfluthrin and deltamethrin; (C) at least one penetrant; (D) at least one vegetable oil; (E) cyclohexanone; (F) at least one nonionic surfactant, at least one anionic surfactant or a mixture thereof; and (G) one or more additives selected from the group consisting of an emulsifier, a foam inhibitor, a preservative, an antioxidant, a spreader, a colorant, a thickener and a mixture thereof. A process for producing the oil-suspension concentrate comprises mixing (A) to (G) with one another and then grinding until an average particle size of less than 10 μm is reached. Also provided is a method of controlling harmful organisms by applying the oil-suspension concentrate to the insects or their habitats.

Oil-based suspension concentrates

The present invention relates to new, oil-based suspension concentrates of active agrochemicals, to a process for producing these formulations and to their use for applying the active substances comprised.

Systemic active agrochemicals, especially systemic insecticides, in order to develop their biological effect, need a formulation which enables the active substances to be taken up into the plant/target organisms. Usually, therefore, systemic active agrochemicals are formulated as an emulsifiable concentrate (EC), soluble liquid (SL) and/or oil-based suspension concentrate (OD). In an EC and SL the active substance is in dissolved form, while in the case of an OD formulation it is a solid. In the latter case the biological action is made possible by the addition of penetrants. Contact actives such as pyrethroids, for example, are formulated preferably as EC, especially when a high initial action is needed. Suspension concentrates (SC) or wettable granules (WG) are technically possible in the majority of cases, but do not display the requisite initial action.

Mixed formulations of systemic and contact insecticides, such as a mixture of imidacloprid with beta-cyfluthrin, for example, are of great interest as an alternative to the organophosphates, which carry high acute toxicity. Mixtures of this kind are appropriate alternatives to the application of organophosphates only if a high initial action is present and if formulations with a high active substance content are present. There are no known EC formulations with high levels both of imidacloprid and of beta-cyfluthrin, since there is no solvent able to dissolve both active substances in appropriate amount. Consequently, only oil-based or water-free suspension concentrates come into consideration.

Numerous water-free suspension concentrates of active agrochemicals have already been disclosed. For instance EP-A 0 789 999 describes formulations of this type which in addition to active substance and oil comprise a mixture of different surfactants – including surfactants which serve as penetrants – and also a hydrophobicized aluminophyllosilicate as thickener. The cited patent describes suitable active substances as being those which have a solubility in oil of less than 5 g/l, preferably less than 1 g/l, in particular less than 0.1 g/l.

From US-A 6 165 940, moreover, non-aqueous suspension concentrates are already known in which besides active agrochemical, penetrant and surfactant or surfactant mixture there is an organic solvent, suitable solvents of this type including liquid paraffin or vegetable oil esters. That invention describes suspension concentrates composed of solid active substance(s) and organic solvents, the active substance being less than moderately soluble. A solubility of less than 10 g/l, preferably less than 5 g/l, is explicitly stated.

DE-A 10 129 855 describes further oil-based suspension concentrates which comprise active agrochemicals, penetrants and surfactants.

A disadvantage of the aforementioned formulations is that it is not possible to develop a sparingly soluble (less than 10 g/l) active substance in combination with a moderately soluble (10 to 50 g/l at room temperature) active substance in the form of a stable oil-based suspension concentrate without the occurrence of crystal growth after storage. The growth of active substance crystals in a formulation is a considerable disadvantage for the user, since it may result in clogging of the screens of his or her spraying equipment when the product is applied.

The present invention relates to stable, storable, oil-based suspension concentrates composed of a sparingly soluble active substance and a moderately soluble active substance which is present in a higher concentration than the solubility limit in the formulation.

New, oil-based suspension concentrates have now been found, comprising

- at least one room-temperature-solid active substance from the class of the neonicotinoids,
- at least one room-temperature-solid active substance from the class of the pyrethroids,
- at least one penetrant,
- at least one vegetable oil,
- cyclohexanone,
- at least one nonionic surfactant and/or at least one anionic surfactant, and
- one or more additives from the groups of the emulsifiers, foam inhibitors, preservatives, antioxidants, spreaders, colorants and/or a thickener.

Suitable penetrants in the present context include all those substances which are usually used to enhance the penetration of active agrochemicals into plants. Penetrants are defined in this context by their ability to penetrate from the aqueous spray liquor and/or from the spray coating into the cuticle of the plant and thereby to increase the mobility of active substances in the cuticle. The method described later on and in the literature (Baur et al., 1997, Pesticide Science 51, 131-152) can be used to determine this property.

Additionally it has been found that the oil-based suspension concentrates of the invention can be produced by mixing

- at least one room-temperature-solid active substance from the class of the neonicotinoids,
- at least one room-temperature-solid active substance from the class of the pyrethroids,
- at least one penetrant,
- at least one vegetable oil,

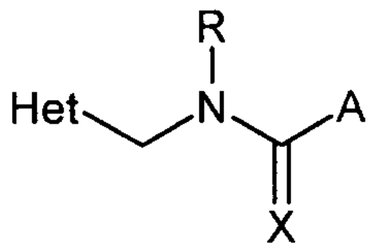
- cyclohexanone,
- at least one nonionic surfactant and/or at least one anionic surfactant, and
- one or more additives from the groups of the emulsifiers, foam inhibitors, preservatives, antioxidants, spreaders, colorants and/or a thickener.

with one another and optionally subsequently grinding the resultant suspension.

Finally it has been found that the oil-based suspension concentrates of the invention are highly suitable for applying the active agrochemicals comprised to plants and/or their habitat.

It is to be considered extremely surprising that the oil-based suspension concentrates of the invention exhibit very good stability, and in particular that no significant crystal growth was observed even after storage at fluctuating temperature. Also unexpected is the fact that they display a markedly better biological activity than the aforementioned formulations most similar in composition. Particularly unexpected is the fact that a very high initial action of the contact substance is found, in spite of the fact that this active substance is present partly as a solid.

Appropriate active substances are insecticides from the class of the neonicotinoids. They are outstandingly suitable for controlling animal pests. Insecticides from the class of the neonicotinoids can be described by formula (II) below



(II)

in which

Het is a heterocycle selected from the following group of heterocycles: 2-chloropyrid-5-yl, 2-methylpyrid-5-yl, 1-oxido-3-pyridino, 2-chloro-1-oxido-5-pyridino, 2,3-dichloro-1-oxido-5-pyridino, tetrahydrofuran-3-yl, 5-methyl-tetrahydrofuran-3yl, 2-chlorothiazol-5-yl,

A is $N(R^1)(R^2)$ or $S(R^2)$,

in which

R^1 is hydrogen, C_1-C_6-alkyl, phenyl-C_1-C_4-alkyl, C_3-C_6-cycloalkyl, C_2-C_6-alkenyl or C_2-C_6-alkynyl and

R^2 is C_1-C_6-alkyl, C_2-C_6-alkenyl, C_2-C_6-alkynyl –C(=O)-CH_3 or benzyl,

R is C_1-C_6-alkyl, C_2-C_6-alkenyl, C_2-C_6-alkynyl –C(=O)-CH_3 or benzyl or together with R^2 is one of the following groups:

-CH_2-CH_2-, -CH_2-CH_2-CH_2-, -CH_2-O-CH_2-, -CH_2-S-CH_2-, -CH_2-NH-CH_2-, -CH_2-N-(CH_3)-CH_2- and

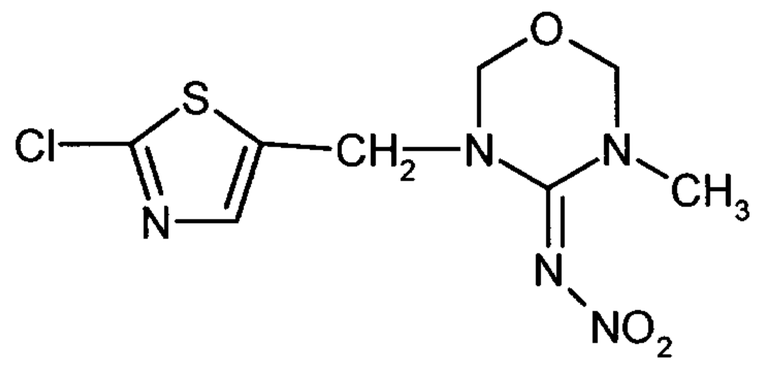
X is N-NO_2, N-CN or CH-NO_2

(see for example EP-A1-192 606, EP-A2-580 533, EP-A2-376 279, EP-A2-235 725).

Mention may be made individually of the following compounds which can be used in accordance with the invention.

One compound used with preference in accordance with the invention is thiamethoxam.

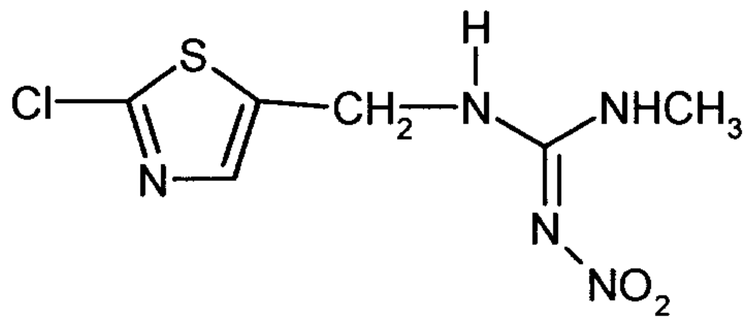
Thiamethoxam has the formula



and is known from EP A2 0 580 533.

A further compound used with preference in accordance with the invention is clothianidin.

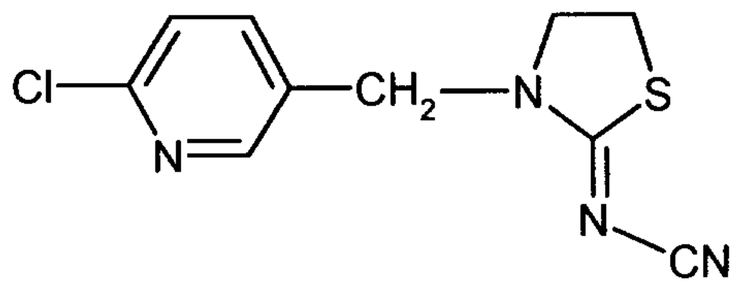
Clothianidin has the formula



and is known from EP A2 0 376 279.

A further compound used with preference in accordance with the invention is thiacloprid.

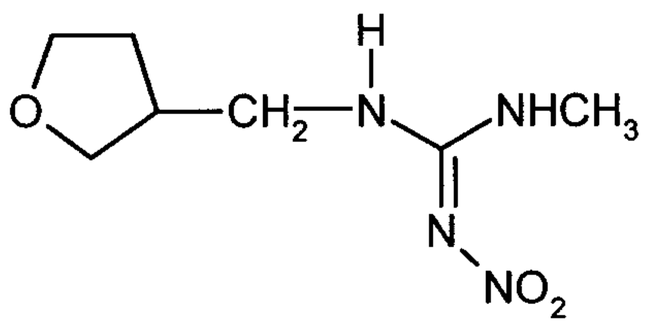
Thiacloprid has the formula



and is known from EP A2 0 235 725.

A further compound used with preference in accordance with the invention is dinotefuran.

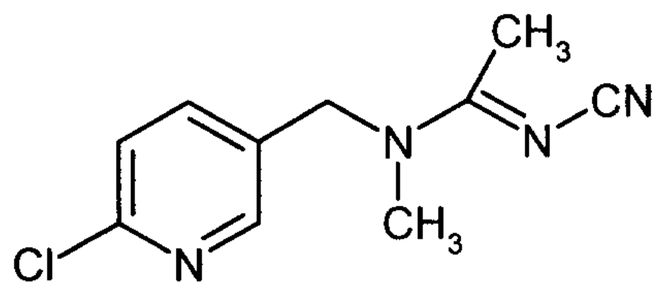
Dinotefuran has the formula



and is known from EP A1 0 649 845.

A further compound used with preference in accordance with the invention is acetamiprid.

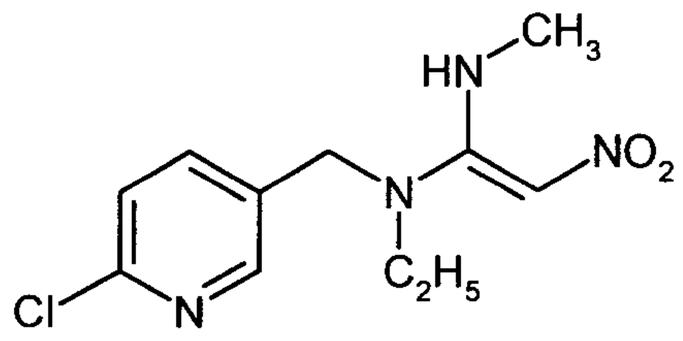
Acetamiprid has the formula



and is known from WO A1 91/04965.

A further compound used with preference in accordance with the invention is nitenpyram.

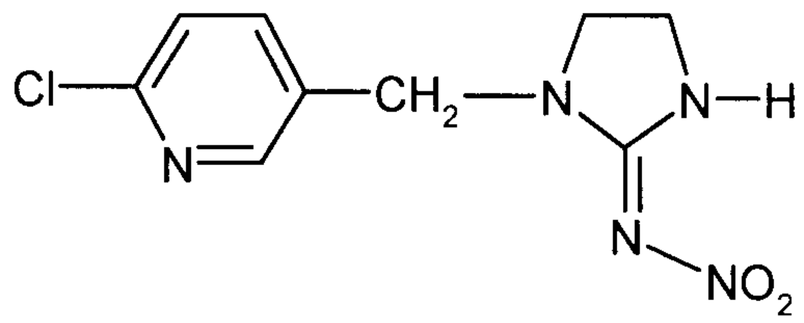
Nitenpyram has the formula



and is known from EP A2 0 302 389.

A further compound used with preference in accordance with the invention is imidacloprid.

Imidacloprid has the formula



and is known from EP 0 192 060.

Particular preference is given to imidacloprid.

Suitable further active substances include those from the group of the pyrethroids, for example acrinathrin, allethrin (d-cis-trans, d-trans), beta-cyfluthrin, bifenthrin, bioallethrin, bioallethrin-S-cyclopentyl isomer, bioethanomethrin, biopermethrin, bioresmethrin, chlovaporthrin, cis-cypermethrin, cis-resmethrin, cis-permethrin, clocythrin, cycloprothrin, cyfluthrin, cyhalothrin, cypermethrin (alpha-, beta-, theta-, zeta), cyphenothrin, deltamethrin, empenthrin (1R-isomer), esfenvalerate, etofenprox, fenfluthrin, fenpropathrin, fenpyrithrin, fenvalerate, flubrocythrinate, flucythrinate, flufenprox, flumethrin, fluvalinate, fubfenprox, gamma-cyhalothrin, imiprothrin, kadethrin, lambda-cyhalothrin, metofluthrin, permethrin (cis-, trans-), phenothrin (1R-trans-isomer), prallethrin, profluthrin, protrifenbute, pyresmethrin, resmethrin, RU 15525, silafluofen, tau-fluvalinate, tefluthrin, terallethrin, tetramethrin (1R isomer), tralomethrin, transfluthrin, ZXI 8901, pyrethrins (pyrethrum). Preference is given to beta-cyfluthrin and deltamethrin.

In one aspect, the invention relates to an oil-suspension concentrate of an agrochemically active product, comprising: (A) imidacloprid; (B) at least one pyrethroid selected from the group consisting of beta-cyfluthrin and deltamethrin; (C) at least one penetrant; (D) at least one vegetable oil; (E) cyclohexanone; (F) at least one nonionic surfactant, at least one anionic surfactant or a mixture thereof; and (G) one or more additives selected from the group consisting of an emulsifier, a foam inhibitor, a preservative, an antioxidant, a spreader, a colorant, a thickener and a mixture thereof.

In a further aspect, the invention relates to a method of controlling harmful insects, comprising applying the oil-suspension concentrate as defined above, neat or diluted, to the insects or their habitat in an amount such that an effective amount of (A) and (B) acts on the insects or their habitat.

Preferred penetrants are alkanol alkoxylates of the formula

$$R\text{-}O\text{-}(\text{-}AO)_mR' \quad (I)$$

in which

R is linear or branched alkyl having 4 to 20 carbon atoms,

R' is H, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl or n-hexyl,

AO is an ethylene oxide radical, a propylene oxide radical, a butylene oxide radical or mixtures of ethylene oxide and propylene oxide radicals or butylene oxide radicals, and

m is a number from 2 to 30.

One particularly preferred group of penetrants are alkanol alkoxylates of the formula

$$R\text{-}O\text{-}(\text{-}EO\text{-})_n\text{-}R' \quad (I\text{-}a)$$

in which

R is as defined above,

R' is as defined above,

EO is $\text{-}CH_2\text{-}CH_2\text{-}O\text{-}$, and

n is a number from 2 to 20.

A further particularly preferred group of penetrants are alkanol alkoxylates of the formula

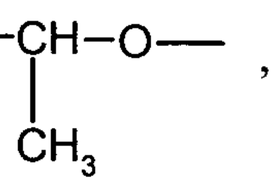
$$R\text{-}O\text{-}(\text{-}EO\text{-})_p\text{-}(\text{-}PO\text{-})_q\text{-}R' \quad (I\text{-}b)$$

in which

R is as defined above,

R' is as defined above,

EO is $\text{-}CH_2\text{-}CH_2\text{-}O\text{-}$,

PO is  ,

p is a number from 1 to 10, and

q is a number from 1 to 10.

A further particularly preferred group of penetrants are alkanol alkoxylates of the formula

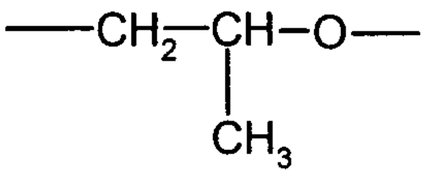
$$R\text{-}O\text{-}(\text{-}PO\text{-})_r\text{-}(EO\text{-})_s\text{-}R' \quad (I\text{-}c)$$

in which

R is as defined above,

R' is as defined above,

EO is $\text{-}CH_2\text{-}CH_2\text{-}O\text{-}$,

PO is  ,

r is a number from 1 to 10, and

s is a number from 1 to 10.

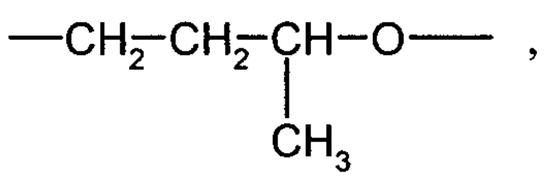
A further particularly preferred group of penetrants are alkanol alkoxylates of the formula (I-e)

$$R\text{-}O\text{-}(\text{-}EO\text{-})_p\text{-}(\text{-}BO\text{-})_q\text{-}R' \quad \text{(I-d)}$$

in which

R and R' are as defined above,

EO is CH_2-CH_2-O-,

BO is  ,

p is a number from 1 to 10, and

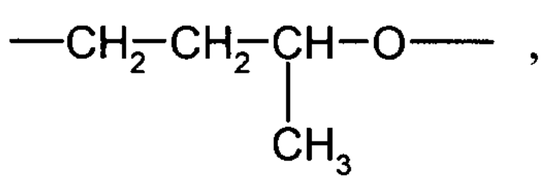
q is a number from 1 to 10.

A further particularly preferred group of penetrants are alkanol alkoxylates of the formula (I-f)

$$R\text{-}O\text{-}(\text{-}BO\text{-})_r\text{-}(\text{-}EO\text{-})_S\text{-}R' \quad \text{(I-e)}$$

in which

R and R' are as defined above,

BO is  ,

EO is CH_2-CH_2-O-,

r is a number from 1 to 10, and

s is a number from 1 to 10.

A further particularly preferred group of penetrants are alkanol alkoxylates of the formula

$$CH_3\text{-}(CH_2)_t\text{-}CH_2\text{-}O\text{-}(\text{-}CH_2\text{-}CH_2\text{-}O\text{-})_u\text{-}R' \qquad \text{(I-f)}$$

in which

R' is as defined above,

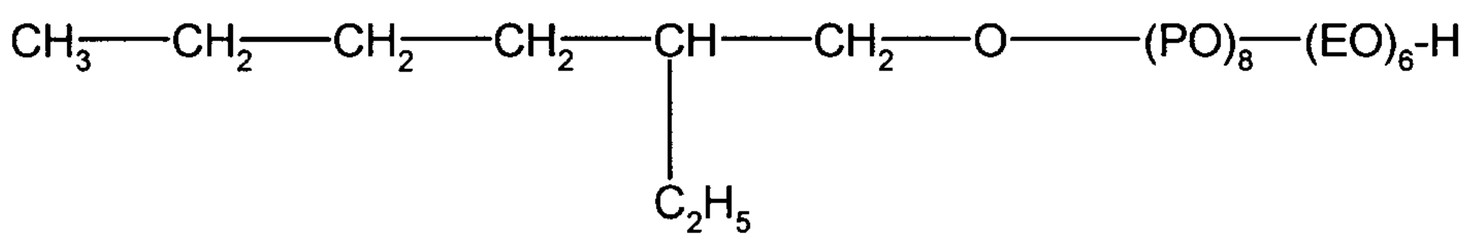
t is a number from 8 to 13, and

u is a number from 6 to 17.

In the formulae given above

R is preferably butyl, isobutyl, n-pentyl, isopentyl, neopentyl, n-hexyl, isohexyl, n-octyl, isooctyl, 2-ethylhexyl, nonyl, isononyl, decyl, n-dodecyl, isododecyl, lauryl, myristyl, isotridecyl, trimethylnonyl, palmityl, stearyl or eicosyl.

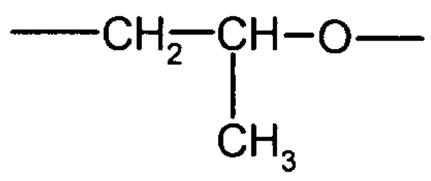
An example that may be mentioned of an alkanol alkoxylate of the formula (I-c) is 2-ethylhexyl alkoxylate of the formula



(I-c-1)

in which

EO is $-CH_2\text{-}CH_2\text{-}O\text{-}$,

PO is  , and

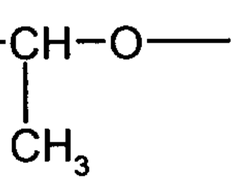
the numbers 8 and 6 represent average values.

An example that may be mentioned of an alkanol alkoxylate of the formula (I-d) is the formula

$$CH_3\text{-}(CH_2)_{10}\text{-}O\text{-}(\text{-}EO\text{-})_6\text{-}(\text{-}BO\text{-})_2\text{-}CH_3 \qquad \text{(I-d-1)}$$

in which

EO is $CH_2\text{-}CH_2\text{-}O\text{-}$,

BO is  , and

the numbers 10, 6 and 2 represent average values.

Particularly preferred alkanol alkoxylates of the formula (I-f) are compounds of this formula in which

t is a number from 9 to 12 and

u is a number from 7 to 9.

With very particular preference mention may be made of alkanol alkoxylate of the formula (I-f-1)

$$CH_3\text{-}(CH_2)_t\text{-}CH_2\text{-}O\text{-}(\text{-}CH_2\text{-}CH_2\text{-}O\text{-})_u\text{-}H' \quad \text{(I-f-1)}$$

in which

t is the average value 10.5 and

u is the average value 8.4.

Mention may likewise be made with very particular preference of alkanol alkoxylate of the formula (I-f-1-1)

$$CH_3\text{-}(CH_2)_t\text{-}CH_2\text{-}O\text{-}(\text{-}CH_2\text{-}CH_2\text{-}O\text{-})_u\text{-}H \qquad \text{(I-f-1-1)}$$

in which

t is the average value 10.5 and

u is the average value 8.4.

A general definition of the alkanol alkoxylates is given by the above formulae. These substances are mixtures of substances of the stated type with different chain lengths. The indices therefore have average values which may also deviate from whole numbers.

The alkanol alkoxylates of the formulae indicated are known or can be prepared by known methods (cf. WO 98-35 553, WO 00-35 278 and EP-A 0 681 865).

Suitable vegetable oils include all oils which can normally be used in agrochemical compositions and can be obtained from plants. Examples that may be mentioned include sunflower oil, rapeseed oil, olive oil, castor oil, colza oil, maize seed oil, cottonseed oil and soybean oil.

The oil-based suspension concentrates of the invention comprise at least one nonionic surfactant or dispersant and/or at least one anionic surfactant or dispersant.

Suitable nonionic surfactants or dispersants include all substances of this type that can normally be used in agrochemical compositions. Preferably mention may be made of polyethylene oxide-polypropylene oxide block copolymers, polyethylene glycol ethers of linear alcohols, reaction products of fatty acids with ethylene oxide and/or propylene oxide, and also polyvinyl alcohol, polyvinylpyrrolidone, copolymers of polyvinyl alcohol and polyvinylpyrrolidone, and copolymers of (meth)acrylic acid and (meth)acrylic esters, and also alkyl ethoxylates and alkylaryl ethoxylates, which optionally may be phosphated and optionally may be utilized with bases, it being possible for mention to be made, by way of example, of sorbitol ethoxylates, and also polyoxyalkylenamine derivatives.

Suitable anionic surfactants include all substances of this type that can normally be used in agrochemical compositions. Preference is given to alkali metal salts and alkaline earth metal salts of alkylsulphonic acids or alkylarylsulphonic acids.

A further preferred group of anionic surfactants or dispersants includes the following salts that are of low solubility in vegetable oil: salts of polystyrenesulphonic acids, salts of polyvinylsulphonic acids, salts of naphthalenesulphonic acid-formaldehyde condensation products, salts of condensation products of naphthalenesulphonic acid, phenolsulphonic acid and formaldehyde, and salts of lignosulphonic acid.

Suitable additives which may be included in the formulations of the invention are emulsifiers, foam inhibitors, preservatives, antioxidants, spreaders, colorants and thickeners.

Preferred emulsifiers are ethoxylated nonylphenols, reaction products of alkylphenols with ethylene oxide and/or propylene oxide, ethoxylated arylalkylphenols, and also ethoxylated and propoxylated arylalkylphenols, and also sulphated or phosphated arylalkyl ethoxylates and/or arylalkyl ethoxy-propoxylates, it being possible to mention, by way of example, sorbitan derivatives, such as polyethylene oxide-sorbitan fatty acid esters and sorbitan fatty acid esters.

Suitable foam inhibitors include all substances that can normally be used for this purpose in agrochemical compositions. Preference is given to silicone oils and magnesium stearate.

Suitable preservatives include all substances that can normally be used for this purpose in agrochemical compositions of this type. Examples that may be mentioned include Preventol® (Bayer AG) and Proxel®.

Suitable antioxidants include all substances that can normally be used for this purpose in agrochemical compositions. Preference is given to butylated hydroxytoluene and/or citric acid.

Suitable spreaders include all substances that can normally be used for this purpose in agrochemical compositions. Preference is given to alkylsiloxanes.

Suitable colorants include all substances that can normally be used for this purpose in agrochemical compositions. Mention may be made, by way of example, of titanium dioxide, pigmentary carbon black, zinc oxide and blue pigments, and also Permanent Red FGR.

Suitable thickeners include all substances that can normally be used for this purpose in agrochemical compositions and which function as thickeners. Preference is given to inorganic particles, such as carbonates, silicates and oxides, and also organic substances, such as urea-formaldehyde condensates. By way of example mention may be made of kaolin, rutile, silicon dioxide, so-called highly disperse silica, silica gels, and also natural and synthetic silicates, and additionally talc.

In one particular embodiment the formulations of the invention may further comprise at least one additional active substance (insecticides, attractants, sterilants, bactericides, acaricides, nematicides, fungicides, growth regulators or herbicides). The insecticides include, for example, carbamates, carboxylic esters, chlorinated hydrocarbons, phenylureas, substances produced by microorganisms, etc.

Examples of particularly favourable co-components include the following:

Fungicides:

Inhibitors of nucleic acid synthesis

benalaxyl, benalaxyl-M, bupirimate, chiralaxyl, clozylacon, dimethirimol, ethirimol, furalaxyl, hymexazol, metalaxyl, metalaxyl-M, ofurace, oxadixyl, oxolinic acid

Inhibitors of mitosis and cell division

benomyl, carbendazim, diethofencarb, fuberidazole, pencycuron, thiabendazole, thiophanat-methyl, zoxamide

Inhibitors of respiratory chain complex I

diflumetorim

Inhibitors of respiratory chain complex II

boscalid, carboxin, fenfuram, flutolanil, furametpyr, mepronil, oxycarboxin, penthiopyrad, thifluzamide

Inhibitors of respiratory chain complex III

azoxystrobin, cyazofamid, dimoxystrobin, enestrobin, famoxadone, fenamidone, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, pyraclostrobin, picoxystrobin

Decouplers

dinocap, fluazinam

Inhibitors of ATP production

Fentin acetate, fentin chloride, fentin hydroxide, silthiofam

Inhibitors of amino acid biosynthesis and protein biosynthesis

andoprim, blasticidin-S, cyprodinil, kasugamycin, kasugamycin hydrochloride hydrate, mepanipyrim, pyrimethanil

Inhibitors of signal transduction

fenpiclonil, fludioxonil, quinoxyfen

Inhibitors of lipid and membrane synthesis

chlozolinate, iprodione, procymidone, vinclozolin

ampropylfos, potassium-ampropylfos, edifenphos, iprobenfos (IBP), isoprothiolane, pyrazophos

tolclofos-methyl, biphenyl

iodocarb, propamocarb, propamocarb hydrochloride

Inhibitors of ergosterol biosynthesis

fenhexamid,

azaconazole, bitertanol, bromuconazole, cyproconazole, diclobutrazole, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, etaconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, furconazole, furconazole-cis, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, paclobutrazole, penconazole, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, uniconazole, voriconazole, imazalil, imazalil sulphate, oxpoconazole, fenarimol, flurprimidol, nuarimol, pyrifenox, triforine, pefurazoate, prochloraz, triflumizole, viniconazole,

aldimorph, dodemorph, dodemorph acetate, fenpropimorph, tridemorph, fenpropidin, spiroxamine,

naftifine, pyributicarb, terbinafine

Inhibitors of cell wall synthesis

benthiavalicarb, bialaphos, dimethomorph, flumorph, iprovalicarb, polyoxins, polyoxorim, validamycin A

Inhibitors of melanin biosynthesis

Carpropamid, diclocymet, fenoxanil, phthalide, pyroquilon, tricyclazole

Resistance induction

acibenzolar-S-methyl, probenazole, tiadinil

Multisite

captafol, captan, chlorothalonil, copper salts such as: copper hydroxide, copper naphthenate, copper oxychloride, copper sulphate, copper oxide, oxine-copper and Bordeaux mixture, dichlofluanid, dithianon, dodine, dodine free base, ferbam, fluorofolpet, guazatine, guazatine acetate, iminoctadine, iminoctadine albesilate, iminoctadine triacetate, mancopper, mancozeb, maneb, metiram, metiram zinc, propineb, sulphur and sulphur preparations containing calcium polysulphide, thiram, tolylfluanid, zineb, ziram

Unknown mechanism

amibromdol, benthiazol, bethoxazin, capsimycin, carvone, chinomethionat, chloropicrin, cufraneb, cyflufenamid, cymoxanil, dazomet, debacarb, diclomezine, dichlorophen, dicloran, difenzoquat, difenzoquat methyl sulphate, diphenylamine, ethaboxam, ferimzone, flumetover, flusulphamide, fluopicolide, fluoroimide, hexachlorobenzene, 8-hydroxy-

quinoline sulphate, irumamycin, methasulphocarb, metrafenone, methyl isothiocyanate, mildiomycin, natamycin, nickel dimethyl dithiocarbamate, nitrothal-isopropyl, octhilinone, oxamocarb, oxyfenthiin, pentachlorophenol and salts, 2-phenylphenol and salts, piperalin, propanosine-sodium, proquinazid, pyrrol nitrin, quintozene, tecloftalam, tecnazene, triazoxide, trichlamide, zarilamid and 2,3,5,6-tetrachloro-4-(methylsulphonyl)pyridine, N-(4-chloro-2-nitrophenyl)-N-ethyl-4-methylbenzenesulphonamide, 2-amino-4-methyl-N-phenyl-5-thiazolecarboxamide, 2-chloro-N-(2,3-dihydro-1,1,3-trimethyl-1H-inden-4-yl)-3-pyridine-carboxamide, 3-[5-(4-chlorophenyl)-2,3-dimethylisoxazolidin-3-yl]pyridine, cis-1-(4-chloro-phenyl)-2-(1H-1,2,4-triazol-1-yl)cycloheptanol, 2,4-dihydro-5-methoxy-2-methyl-4-[[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3H-1,2,3-triazol-3-one (185336-79-2), methyl 1-(2,3-dihydro-2,2-dimethyl-1H-inden-1-yl)-1H-imidazole-5-carboxylate, 3,4,5-trichloro-2,6-pyridinedicarbonitrile, methyl 2-[[[cyclopropyl[(4-methoxy-phenyl)imino]methyl]thio]methyl]-.alpha.-(methoxymethylene)benzacetate, 4-chloro-alpha-propynyloxy-N-[2-[3-methoxy-4-(2-propynyloxy)phenyl]ethyl]benzacetamide, (2S)-N-[2-[4-[[3-(4-chlorophenyl)-2-propynyl]oxy]-3-methoxyphenyl]ethyl]-3-methyl-2-[(methylsulphon-yl)amino]butanamide, 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)[1,2,4]-triazolo[1,5-a]pyrimidine, 5-chloro-6-(2,4,6-trifluorophenyl)-N-[(1R)-1,2,2-trimethylpropyl]-[1,2,4]triazolo[1,5-a]pyrimidin-7-amine, 5-chloro-N-[(1R)-1,2-dimethylpropyl]-6-(2,4,6-trifluorophenyl)[1,2,4]triazolo[1,5-a]pyrimidin-7-amine, N-[1-(5-bromo-3-chloropyridin-2-yl)ethyl]-2,4-dichloronicotinamide, N-(5-bromo-3-chloropyridin-2-yl)methyl-2,4-dichloro-nicotinamide, 2-butoxy-6-iodo-3-propylbenzopyranon-4-one, N-{(Z)-[(cyclopropylmethoxy)-imino][6-(difluoromethoxy)-2,3-difluorophenyl]methyl}-2-benzacetamide, N-(3-ethyl-3,5,5-trimethylcyclohexyl)-3-formylamino-2-hydroxybenzamide, 2-[[[[1-[3(1-fluoro-2-phenyl-ethyl)oxy]phenyl]ethylidene]amino]oxy]methyl]-alpha-(methoxyimino)-N-methyl-alpha-benzacetamide, N-{2-[3-chloro-5-(trifluoromethyl)pyridin-2-yl]ethyl}-2-(trifluoro-methyl)benzamide, N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide, N-(6-methoxy-3-pyridinyl)cyclopropanecarboxamide, 1-[(4-methoxyphenoxy)methyl]-2,2-dimethylpropyl-1H-imidazole-1-carboxylic acid, O-[1-[(4-methoxyphenoxy)methyl]-2,2-dimethylpropyl]-1H-imidazole-1-carbothioic acid, 2-(2-{[6-(3-chloro-2-methylphenoxy)-5-fluoropyrimidin-4-yl]oxy}phenyl)-2-(methoxyimino)-N-methyl-acetamide

Bactericides:

bronopol, dichlorophen, nitrapyrin, nickel dimethyldithiocarbamate, kasugamycin, octhilinone, furancarboxylic acid, oxytetracycline, probenazole, streptomycin, tecloftalam, copper sulphate and other copper preparations.

Insecticides/acaricides/nematicides:

Acetylcholine esterase (AChE) inhibitors

Carbamates,

for example alanycarb, aldicarb, aldoxycarb, allyxycarb, aminocarb, bendiocarb, benfuracarb, bufencarb, butacarb, butocarboxim, butoxycarboxim, carbaryl, carbofuran, carbosulphan, cloethocarb, dimetilan, ethiofencarb, fenobucarb, fenothiocarb, formetanate, furathiocarb, isoprocarb, metam-sodium, methiocarb, methomyl, metolcarb, oxamyl, pirimicarb, promecarb, propoxur, thiodicarb, thiofanox, trimethacarb, XMC, xylylcarb triazamate

Organophosphates,

for example acephate, azamethiphos, azinphos (-methyl, -ethyl), bromophos-ethyl, bromfenvinfos (-methyl), butathiofos, cadusafos, carbophenothion, chlorethoxyfos, chlorfenvinphos, chlormephos, chlorpyrifos (-methyl/-ethyl), coumaphos, cyanofenphos, cyanophos, chlorfenvinphos, demeton-S-methyl, demeton-S-methylsulphon, dialifos, diazinon, dichlofenthion, dichlorvos/DDVP, dicrotophos, dimethoate, dimethylvinphos, dioxabenzofos, disulphoton, EPN, ethion, ethoprophos, etrimfos, famphur, fenamiphos, fenitrothion, fensulphothion, fenthion, flupyrazofos, fonofos, formothion, fosmethilan, fosthiazate, heptenophos, iodofenphos, iprobenfos, isazofos, isofenphos, isopropyl O-salicylate, isoxathion, malathion, mecarbam, methacrifos, methamidophos, methidathion, mevinphos, monocrotophos, naled, omethoate, oxydemeton-methyl, parathion (-methyl/-ethyl), phenthoate, phorate, phosalone, phosmet, phosphamidon, phosphocarb, phoxim, pirimiphos (-methyl/-ethyl), profenofos, propaphos, propetamphos, prothiofos, prothoate, pyraclofos, pyridaphenthion, pyridathion, quinalphos, sebufos, sulphotep, sulprofos, tebupirimfos, temephos, terbufos, tetrachlorvinphos, thiometon, triazophos, triclorfon, vamidothion

Sodium channel modulators / voltage-dependent sodium channel blockers

DDT

Oxadiazines,

for example indoxacarb

Acetylcholine receptor agonists/antagonists

Chloronicotinyls,

for example acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, nithiazine, thiacloprid, thiamethoxam

Nicotine, bensultap, cartap

Acetylcholine receptor modulators

Spinosyns,

for example spinosad

GABA-controlled chloride channel antagonists

Organochlorines,

for example camphechlor, chlordane, endosulphan, gamma-HCH, HCH, heptachlor, lindane, methoxychlor

Fiprols,

for example acetoprole, ethiprole, fipronil, pyrafluprole, pyriprole, vaniliprole

Chloride channel activators

Mectins,

for example avermectin, emamectin, emamectin-benzoate, ivermectin, milbemycin

Juvenile hormone mimetics,

for example diofenolan, epofenonane, fenoxycarb, hydroprene, kinoprene, methoprene, pyriproxifen, triprene

Ecdysone agonists/disruptors

Diacylhydrazines,

for example chromafenozide, halofenozide, methoxyfenozide, tebufenozide

Chitin biosynthesis inhibitors

Benzoylureas,

for example bistrifluron, chlofluazuron, diflubenzuron, fluazuron, flucycloxuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, noviflumuron, penfluron, teflubenzuron, triflumuron

Buprofezin

Cyromazine

Oxidative phosphorylation inhibitors, ATP disruptors

Diafenthiuron

Organotin compounds,

for example azocyclotin, cyhexatin, fenbutatin-oxide

Oxidative phosphorylation decouplers acting by interrupting the H-proton gradient

Pyrroles,

for example chlorfenapyr

Dinitrophenols,

for example binapacyrl, dinobuton, dinocap, DNOC

Site-I electron transport inhibitors

METI's,

for example fenazaquin, fenpyroximate, pyrimidifen, pyridaben, tebufenpyrad, tolfenpyrad

Hydramethylnon

Dicofol

Site-II electron transport inhibitors

Rotenone

Site-III electron transport inhibitors

Acequinocyl, fluacrypyrim

Microbial disruptors of the insect gut membrane

Bacillus thuringiensis strains

Lipid synthesis inhibitors

Tetronic acids,

for example spirodiclofen, spiromesifen

Tetramic acids,

for example spirotetramate (CAS Reg. No.: 203313-25-1) and 3-(2,5-dimethylphenyl)-8-methoxy-2-oxo-1-azaspiro[4.5]dec-3-en-4-yl ethyl carbonate (alias: carbonic acid, 3-(2,5-dimethylphenyl)-8-methoxy-2-oxo-1-azaspiro[4.5]dec-3-en-4-yl ethyl ester, CAS Reg. No.: 382608-10-8)

Carboxamides,

for example flonicamid

Octopaminergic agonists,

for example amitraz

Inhibitors of magnesium-stimulated ATPase,

Propargite

Benzodicarboxamides,

for example flubendiamide

Nereistoxin analogues,

for example thiocyclam hydrogen oxalate, thiosultap-sodium

Biologicals, hormones or pheromones,

azadirachtin, Bacillus spec., Beauveria spec., codlemone, Metarrhizium spec., Paecilomyces spec., thuringiensin, Verticillium spec.

Active compounds with unknown or unspecific mechanisms of action

Fumigants,

for example aluminium phosphide, methyl bromide, sulphuryl fluoride

Antifeedants,

for example cryolite, flonicamid, pymetrozine

Mite growth inhibitors,

for example clofentezine, etoxazole, hexythiazox

amidoflumet, benclothiaz, benzoximate, bifenazate, bromopropylate, buprofezin, quinomethionate, chlordimeform, chlorobenzilate, chloropicrin, clothiazoben, cycloprene, cyflumetofen, dicyclanil, fenoxacrim, fentrifanil, flubenzimine, flufenerim, flutenzin, gossyplure, hydramethylnone, japonilure, metoxadiazone, petroleum, piperonyl butoxide, potassium oleate, pyridalyl, sulphluramid, tetradifon, tetrasul, triarathene, verbutin

The amount of the individual components can be varied within a relatively wide range in the oil-based suspension concentrates of the invention. Thus the concentrations

- of active agrochemicals are between 5% and 40%, preferably between 10% and 37.5%, very preferably between 12.5% and 35% by weight,
- of penetrant are between 5% and 55%, preferably between 10% and 35% by weight,
- of vegetable oil are between 15% and 55%, preferably between 20% and 50% by weight,
- of cyclohexanone are between 5% and 20%, preferably between 7% and 16% by weight,
- of surfactants and/or dispersants are between 2.5% and 30%, preferably between 5.0% and 25% by weight, and
- of additives are between 0.1% and 25%, preferably between 0.1% and 20% by weight.

The oil-based suspension concentrates of the invention are produced by mixing the components with one another in the respectively desired proportions. The order in which the constituents are

combined with one another is arbitrary. Suitably, the penetrant and the vegetable oil are mixed initially and the remaining ingredients of the mixture are added. Appropriately the solid components are used in a finely ground state. It is, however, also possible to subject the suspension which results after the constituents have been combined first to a coarse grinding and then to a fine grinding, so that the mean particle size is below 20 µm. Preferred suspension concentrates are those in which the solid particles have a mean size between 1 and 10 µm.

The temperatures when carrying out the process of the invention can be varied within a certain range. The work is carried out generally at temperatures between 10°C and 60°C, preferably between 15°C and 40°C.

Equipment suitable for carrying out the process of the invention includes customary mixing and grinding apparatus which is used for producing agrochemical formulations.

The oil-based suspension concentrates of the invention constitute formulations which remain stable even following prolonged storage at elevated temperatures or in the cold, since no significant crystal growth is observed. By dilution with water they can be converted into homogeneous spray liquids. These spray liquids are applied by customary methods, i.e., for example, by spraying, pouring or injecting.

The application rate of the oil-based suspension concentrates of the invention can be varied within a relatively wide range. It is guided by the particular active agrochemicals and by their amount in the formulations.

With the aid of the oil-based suspension concentrates of the invention it is possible to deliver active agrochemicals particularly from the class of the neonicotinoids, to plants and/or their habitat in a particularly advantageous way.

With the formulations of the invention it is possible to treat all plants and plant parts. By plants here are meant all plants and plant populations, such as desirable and unwanted wild plants or crop plants (including naturally occurring crop plants). Crop plants may be plants

which can be obtained by conventional breeding and optimization methods or by biotechnological and gene-technological methods or combinations of these methods, including the transgenic plants and including the plant cultivars which can or cannot be protected by varietal property rights. By plant parts are to be meant all above-ground and below-ground parts and organs of the plants, such as shoot, leaf, flower and root, an exemplary listing embracing leaves, needles, stems, trunks, flowers, fruit bodies, fruits and seeds and also roots, tubers and rhizomes. The plant parts also include harvested material and also vegetative and generative propagation material, examples being seedlings, tubers, rhizomes, cuttings and seeds.

What may be emphasized in this context is the particularly advantageous effect of the compositions according to the invention with regard to their use in cereal plants such as, for example, wheat, oats, barley, spelt, triticale and rye, but also in maize, sorghum and millet, rice, sugar cane, soya beans, sunflowers, potatoes, cotton, oilseed rape, canola, tobacco, sugar beet, fodder beet, asparagus, hops and fruit plants (comprising pome fruit such as, for example, apples and pears, stone fruit such as, for example, peaches, nectarines, cherries, plums and apricots, citrus fruits such as, for example, oranges, grapefruits, limes, lemons, kumquats, tangerines and satsumas, nuts such as, for example, pistachios, almonds, walnuts and pecan nuts, tropical fruits such as, for example, mango, papaya, pineapple, dates and bananas, and grapes) and vegetables (comprising leaf vegetables such as, for example, endives, corn salad, Florence fennel, lettuce, cos lettuce, Swiss chard, spinach and chicory for salad use, cabbages such as, for example, cauliflower, broccoli, Chinese leaves, Brassica oleracea (L.) convar. acephala var. sabellica L. (curly kale, feathered cabbage), kohlrabi, Brussels sprouts, red cabbage, white cabbage and Savoy cabbage, fruit vegetables such as, for example, aubergines, cucumbers, capsicums, table pumpkins, tomatoes, courgettes and sweetcorn, root vegetables such as, for example celeriac, wild turnips, carrots, including yellow cultivars, Raphanus sativus var. niger and var. radicula, beetroot, scorzonera and celery, legumes such as, for example, peas and beans, and vegetables from the Allium family such as, for example, leeks and onions).

The treatment of the plants and plant parts in accordance with the invention with the inventive formulations is carried out directly or by action on their environment, habitat or storage area in accordance with the customary treatment methods, for example by dipping, spraying, vaporizing, atomizing, broadcasting or painting on and, in the case of propagation material, especially seeds, additionally by single or multiple coating.

The active agrochemicals comprised develop a better biological activity than when applied in the form of the corresponding conventional formulations.

Figure 1: illustrates the result of a flow test with inventive formulation 16, measured over 40 cycles.

Figure 2: illustrates the result of a flow test with comparative formulation 3, measured over 4 cycles.

Figure 3: is light-microscope investigation of Comparative Example 3 after eight-week storage.

Figure 4: is light-microscope investigation of Comparative Example 1 after eight-week storage.

Figure 5: is light-microscope investigation of inventive formulation 16 after eight-week storage.

The invention is illustrated by the following examples.

Examples

Preparation Examples

Example 1

To prepare a suspension concentrate

144.0	G	of imidacloprid
38.4	G	of deltamethrine
100.0	G	of Arlatone® T
75.0	G	of cyclohexanone
130.0	G	of Atlox® 3467
20.0	G	of lignosulphonate (Borresperse® NA)
25.0	G	of propylene glycol
0.5	G	of polydimethylsiloxane
2.0	G	of anhydrous citric acid
2.0	G	of 2,6-di-tert-butyl-4-methylphenol

are introduced with stirring at room temperature into a mixture of

200.0	G	of the compound of formula (I-c-1) and
263.1	G	of sunflower oil

After the end of the addition the mixture is stirred at room temperature for a further 10 minutes. The resultant homogeneous suspension is subjected first to coarse grinding and then to fine grinding, giving a suspension in which 90% of the solid particles have a size below 6 µm.

The formulas below were produced in the same way as for Example 1.

Table 1

	2	3	4	5	6	7	8	9	10
Beta-Cyfluthrin		85.5		46.5	84	84	84	85.5	84
Deltamethrin	38.5		38.5						
Imidacloprid	144	198	144	102	196	196	196	198	196
Thiacloprid									
2,6-Di-tert-butyl-4-Methylphenol	2	2	2	2	2	2	2	2	2
Agnique ® KE 3552		150							
Arlatone ® T	100	100		100	100	100	100	100	100
Atlox ® 3467			113						
Atlox ® 4894	50	50		50	80	50		50	
Atlox ® 4913 (anhydrous)									
Atlox ® 4914							50		50
Borresperse ® NA			20						5
Cyclohexanone	75	150	75	75	100	100	150	150	150
Genagen ® 4166									
Kraftsperse ® DW 5						5			
Maize oil	383								
Morwet ® D 425	5	5		5			5	5	
N-Methylpyrrolidone									
Polydimethylsiloxane	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Propylene glycol			25						
Solvesso ® 100									
Sunflower oil		257	280	417	235.5	260.5	260.5	257	260.5
Trylox ® 6746			100						
Compound (I-c-1)	200		200	200	200	200	150		150
Compound (I-d-1)									
Compound (I-f-1)								150	
Anhydrous citric acid	2	2	2	2	2	2	2	2	2

Table 1 (continued):

	11	12	13	14	15	16	17	18	19	20
Beta-Cyfluthrin		46.5	46.5	85.5		85.5				85.5
Deltamethrin	38.5				38.5		38.5	38.5	72.5	
Imidacloprid	144	102	102	198	144	198	144	144		198
Thiacloprid									143	
2,6-Di-tert-butyl-4-Methylphenol	2	2	2	2	2	2	2	2	2	2
Agnique ® KE 3552	200									
Arlatone ® T	100	100	100		100	100		100	100	100
Atlox ® 3467		113			130		130		110	
Atlox ® 4894	50			50		50		50		50
Atlox ® 4913 (anhydrous)					30					
Atlox ® 4914			50							
Borresperse ® NA					30					
Cyclohexanone	75	75	75	150	75	150	100	75	125	150
Genagen ® 4166										
Kraftsperse ® DW 5										
Maize oil			417							
Morwet ® D 425	5		5	5		5		5		5
N-Methylpyrrolidone										
Polydimethylsiloxane	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Propylene glycol					25					
Solvesso ® 100										
Sunflower oil	383	359		257	223	257	283	383	245	257
Trylox ® 6746				100			100			
Compound (I-c-1)		200	200	150	200	150	200		200	
Compound (I-d-1)								200		150
Compound (I-f-1)										
Anhydrous citric acid	2	2	2	2	2	2	2	2	2	2

Table 1 (continued):

	21	22	23	24	25
Beta-Cyfluthrin			84	46.5	85.5
Deltamethrin	72.5	38.5			
Imidacloprid		144	196	102	198
Thiacloprid	143				
2,6-Di-tert-butyl-4-methylphenol	2	2	2	2	2
Agnique ® KE 3552					
Arlatone ® T	100	100	75	100	100
Atlox ® 3467				113	
Atlox ® 4894	50	50			50
Atlox ® 4913 (anhydrous)					
Atlox ® 4914			50		
Borresperse ® NA			20		
Cyclohexanone	125	75	200	75	150
Genagen ® 4166					
Kraftsperse ® DW 5					
Maize oil					
Morwet ® D 425	5	5			5
N-Methylpyrrolidone					
Polydimethylsiloxane	0.5	0.5	0.5	0.5	0.5
Propylene glycol					
Solvesso ® 100					
Sunflower oil	300	383	220.5	359	257
Trylox ® 6746					
Compound (I-c-1)	200	200	150		
Compound (I-d-1)				200	
Compound (I-f-1-1)					150
Anhydrous citric acid	2	2	2	2	2

Comparative Examples

The formulas below were produced in the same way as for Example 1.

Table 2

	1	2	3	4	5	6	7
Beta-Cyfluthrin			94.5	46.5	85.5	85.5	85.5
Deltamethrin	39.5	94.5					
Imidacloprid	147	187	187	102	198	198	198
Thiacloprid							
2,6-Di-tert-butyl-4-methylphenol	2	2	2	2	2	2	2
Agnique ® KE 3552							
Arlatone ® T	100	100	100	100	100	100	100
Atlox ® 3467	130	130	130	113			
Atlox ® 4894					50	50	50
Atlox ® 4913 (anhydrous)							
Atlox ® 4914							
Borresperse ® NA		20					
Cyclohexanone							
Genagen ® 4166							150
Kraftsperse ® DW 5							
Maize oil							
Morwet ® D 425			20		5	5	5
N-Methylpyrrolidone						150	
Polydimethylsiloxane	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Propylene glycol							
Solvesso ® 100				75	150		
Sunflower oil	379	264	264	359	257	257	257
Trylox ® 6746							
Compound (I-c-1)	200	200	200	200	150	150	150
Compound (I-d-1)							
Compound (I-f-1)							
Anhydrous citric acid	2	2	2	2	2	2	2

The components in the compositions of the invention that are defined by means of their trade names are available from the following suppliers:

Trade name	Type of compound	Supplier
Agnique ® KE 3552	alkanol alkoxylate	Cognis
Arlatone ® T	PEG-40 sorbitan peroleate, nonionic	Uniqema
Atlox ® 3467	blend containing alkylaryl sulphonate, ethylhexanol, ethoxylated alcohol	Uniqema
Atlox ® 4894	polyalkoxylated alcohol	Uniqema
Atlox ® 4913 (anhydrous)	polymeric nonionic surfactant	Uniqema
Atlox ® 4914	polymeric nonionic surfactant	Uniqema
Borresperse ® NA	lignosulphonate	Borregaard LignoTech
Genagen ® 4166	caprylic/capric fatty acid dimethylamide	Clariant
Kraftsperse ® DW 5	lignosulphonate, sodium salt	Westvaco
Morwet ® D 425	naphthalene sulphonate	Witco
Solvesso ® 100	aromatic organic solvent	Exxon Mobile
Trylox ® 6746	PEG-40 sorbitol hexaoleate	Cognis

Crystallization behaviour

The crystallization behaviour is investigated by storing 100 ml of formulation for eight weeks under fluctuating temperature conditions. The temperature conditions are as follows:

- 48 hours at 30°C,
- reduction in temperature over 22.5 hours at 2°C/hour down to –15°C,
- 75 hours at –15°C,
- increase in temperature over 22.5 hours at 2°C/hour up to 30°C.

Following storage, the sample is brought to room temperature and the crystallization behaviour is examined.

The crystallization properties are tested by pumping 500 ml in each case of an aqueous spray liquor with a concentrate content of 0.5% by weight in circulation in a flow-traversed apparatus,

by means of a pump, through a fine-meshed screen for 30 minutes. In the course of this procedure the flow over the screen is measured. At the same level of flow, forty repetitions of this operation are carried out, with 500 ml of freshly employed spray liquor in each case. Crystal growth in the formulations tested will lead to blocking of the screen and so will cause a loss of flow over the screen. If the flow is below 20%, the measurement cycle is discontinued. By way of example, 2 results are reproduced as graphs. Graph 1 shows the result of a flow test with an inventive formulation, for which the flow is still unchanged after forty cycles (20 hours). Graph 2 shows the result for a comparative formula. After four cycles (2 hours) the flow has dropped to 20% (see Figures 1 and 2).

Figure 1: result of a flow test with inventive formulation 16, measured over 40 cycles

Figure 2: result of a flow test with comparative formulation 3, measured over 4 cycles

Use Example II: Crystallization behaviour

After eight weeks of storage of the formulation under fluctuating temperature conditions at 54°C the growth of the active substance crystals is determined by means of light microscopy. Immediately after production, all formulations exhibit particle sizes of up to 10 micrometres. All of the inventive formulations exhibit particle sizes after storage of up to a maximum of 20 micrometres. The comparative formulations exhibit substantially coarser particles, up to more than 100 micrometres (see Figures 3 to 5).

Figure 3: light-microscope investigation of Comparative Example 3 after above-described eight-week storage

Figure 4: light-microscope investigation of Comparative Example 1 after above-described eight-week storage

Figure 5: light-microscope investigation of inventive formulation 16 after above-described eight-week storage

Examples of biological action

Knock-down action: Myzus persicae test

An appropriate application solution is produced by diluting 1 part by weight of formulated product with water to the desired concentratrion.

Pepper plants (*Capsicum annuum*) infested by all stages of the green peach aphid (*Myzus persicae*) are sprayed with an application solution at the desired concentration.

Immediately after the spray coating has dried off the action is measured in %. 100% means that all of the aphids have been damaged; 0% means that no aphids have been damaged.

In this test the following formulations, for example, exhibit superior activity over the prior art: 15, 16.

Table 3

Phytopathogenic insects

Myzus persicae test

Active substance/Product	Concentration in g ai/ha	Kill in % after 2h
Example 16 inventive	**1 + 0.43**	**80**
Example 15 inventive	**1 + 0.27**	**90**
Imidacloprid OD 200 prior art	**1**	**60**
ß-Cyfluthrin EC 100 prior art	**0.43**	**50**
ß-Cyfluthrin SC 125 prior art	**0.43**	**20**
Deltamethrin EC 025 prior art	**0.27**	**80**
Deltamethrin SC 200 prior art	**0.27**	**0**

Mortality/efficacy: Myzus persicae test

An appropriate application solution is produced by diluting 1 part by weight of formulated product with water to the desired concentratrion.

Pepper plants (*Capsicum annuum*) infested by all stages of the green peach aphid (*Myzus persicae*) are sprayed with an application solution at the desired concentration.

After the desired time the action is measured in %. 100% means that all of the aphids have been killed; 0% means that no aphids have been killed.

In this test the following formulations, for example, exhibit superior activity over the prior art: 15, 16.

Table 4

Phytopathogenic insects

Myzus persicae test

Active substance/Product	Concentration in g ai/ha	Kill in % after 1d
Example 16 inventive	**1 + 0.43**	**100**
Example 15 inventive	**1 + 0.27**	**98**
Imidacloprid OD 200 prior art	**1**	**94**
ß-Cyfluthrin EC 100 prior art	**0.43**	**55**
ß-Cyfluthrin SC 125 prior art	**0.43**	**20**
Deltamethrin EC 025 prior art	**0.27**	**94**
Deltamethrin SC 200 prior art	**0.27**	**0**

Test description: penetrants at the level of the cuticle

Additives which act as penetrants at the level of the cuticle may be referred to below as accelerator additives (cf. Schönherr and Baur, 1994, Pesticide Science 42, 185-208). The characterizing feature of accelerator additives is their ability to penetrate from the aqueous spray liquor and/or from the spray coating into the cuticle and thereby to increase the mobility of active substances in the cuticle. Other additives such as polyethylene glycol, in contrast, act only in the spray coating (via the liquid phase) or act only as wetting agents, such as sodium dodecyl sulphate, for example.

This test determines the influence of additives on the penetration properties of other substances at the level of the cuticle. The mobility of a test substance in the cuticle is measured with and without an additive, via a desorption method. The method is published in detail in the literature (Baur et al., 1997, Pesticide Science, 51, 131-152), and only the principles and deviations are described below.

As a test substance with the function of a tracer a selection was made here of a radiolabelled weak organic acid. Plant material used comprised the enzymatically isolated leaf cuticles of the top face of peach leaves from outdoor trees. The cuticles were installed in specially manufactured stainless steel diffusion cells. The tracer, in a citrate buffer at a pH of 3 in the dissolved state, was applied to the side originally facing the inside of the leaf. This inner side readily takes up the small radioactive amount of the tracer in the undissociated acid form. Subsequently this inner side was covered and maintained at 100% atmospheric humidity. The morphological outer side of the leaf cuticle, normally exposed to the air, was then contacted with a buffer (pH 7), with the receptor solution, and desorption was started. The penetrated acid form of the test substance is dissociated by the receptor and the desorption follows first-order kinetics. The desorption constant is proportional to the mobility of the tracer in the cuticle.

After at least 2 times for determining this constant, desorption is then continued with a buffer which additionally includes the test additive. Depending on the property of the additive there is then sorption of the additive in the cuticle and, depending on its activity as a plasticizer for the cuticle, there is an increase in the mobility of the tracer within the cuticle. This is manifested in an increased desorption constant, and the ratio of the slopes with additive to the slope without additive describes the effect of the additive to act as a penetrant at the level of the cuticle. The comparison of the average effect of different additives shows their effectiveness to act as cuticle plasticizers.

30725-1110

CLAIMS:

1. An oil-suspension concentrate of an agrochemically active product, comprising:

(A) imidacloprid;

(B) at least one pyrethroid selected from the group consisting of beta-cyfluthrin and deltamethrin;

(C) at least one penetrant;

(D) at least one vegetable oil;

(E) cyclohexanone;

(F) at least one nonionic surfactant, at least one anionic surfactant or a mixture thereof; and

(G) one or more additives selected from the group consisting of an emulsifier, a foam inhibitor, a preservative, an antioxidant, a spreader, a colorant, a thickener and a mixture thereof.

2. The composition according to claim 1, wherein the penetrant is an alkanol alkoxylate of the formula (I):

$$R\text{-}O\text{-}(\text{-}AO)_mR' \quad (I)$$

wherein:

R is linear or branched alkyl having 4 to 20 carbon atoms;

R' is H, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl or n-hexyl;

AO is an ethylene oxide radical, a propylene oxide radical, a butylene oxide radical, or a mixture of ethylene oxide and propylene oxide radicals or butylene oxide radicals; and

m is a number from 2 to 30.

3. The composition according to claim 2, wherein the penetrant is an alkanol alkoxylate of the formula (I-a), (I-b), (I-c), (I-d), (I-e) or (I-f):

$$R\text{-}O\text{-}(\text{-}EO\text{-})_n\text{-}R' \qquad \text{(I-a)}$$

$$R\text{-}O\text{-}(\text{-}EO\text{-})_p\text{-}(\text{-}PO\text{-})_q\text{-}R' \qquad \text{(I-b)}$$

$$R\text{-}O\text{-}(\text{-}PO\text{-})_r\text{-}(EO\text{-})_s\text{-}R' \qquad \text{(I-c)}$$

$$R\text{-}O\text{-}(\text{-}EO\text{-})_p\text{-}(\text{-}BO\text{-})_q\text{-}R' \qquad \text{(I-d)}$$

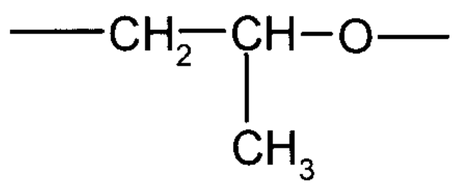
$$R\text{-}O\text{-}(\text{-}BO\text{-})_r\text{-}(\text{-}EO\text{-})_s\text{-}R' \qquad \text{(I-e)}$$

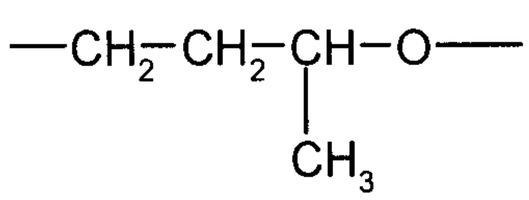
$$CH_3\text{-}(CH_2)_t\text{-}CH_2\text{-}O\text{-}(\text{-}CH_2\text{-}CH_2\text{-}O\text{-})_u\text{-}R' \qquad \text{(I-f)}$$

wherein:

R and R' are as defined in claim 2;

EO is $\text{-}CH_2\text{-}CH_2\text{-}O\text{-}$;

PO is  ;

BO is  ;

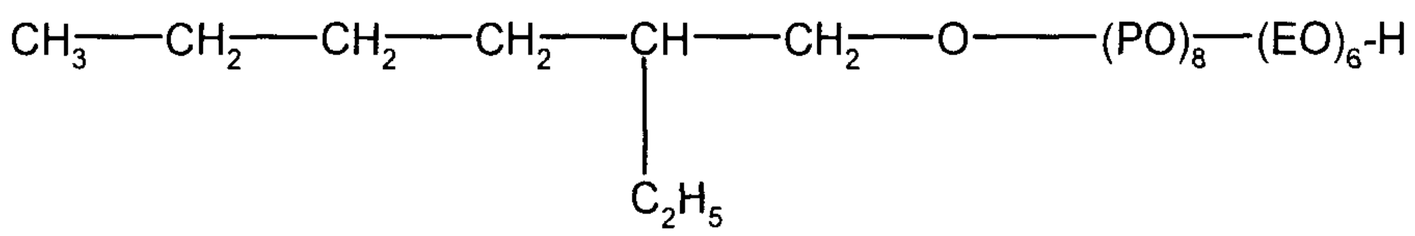
n is a number from 2 to 20;

p, q, r and s are numbers from 1 to 10;

t is a number from 8 to 13; and

u is a number from 6 to 17.

4. The composition according to claim 3, wherein the penetrant is an alkanol alkoxylate of the formula (I-c-1), (I-d-1) or (I-f-1):



(I-c-1)

wherein the numbers 8 and 6 are average values;

CH_3-$(CH_2)_{10}$-O-(-EO-)$_6$-(-BO-)$_2$-CH_3 (I-d-1)

wherein the numbers 10, 6 and 2 are average values; or

CH_3-$(CH_2)_{10.5}$-CH_2-O-(-CH_2-CH_2-O-)$_{8.4}$-H (I-f-1)

wherein the numbers 10.5 and 8.4 are average values.

5. The composition according to claim 3, wherein the penetrant is an alkanol alkoxylate of the formula (I-f-1-1):

CH_3-$(CH_2)_{10.5}$-CH_2-O-(-CH_2-CH_2-O-)$_{8.4}$-H (I-f-1-1)

wherein the numbers 10.5 and 8.4 are average values.

6. The composition according to any one of claims 1 to 5, which comprises:

between 5% and 40% by weight of (A) and (B);

between 5% and 55% by weight of (C);

between 15% and 55% by weight of (D);

between 5% and 20% by weight of (E);

between 2.5% and 30% by weight (F); and

between 0.1% and 25% by weight of (G).

7. The composition according to claim 6, which comprises:

between 10% and 37.5% by weight of (A) and (B);

between 10% and 35% by weight of (C);

between 20% and 50% by weight of (D);

between 7% and 16% by weight of (E);

between 5% and 25% by weight of (F); and

between 0.1% and 20% by weight of (G).

8. A process for producing the oil-suspension concentrate as defined in any one of claims 1 to 7, comprising mixing (A) to (G) with one another and then grinding until an average particle size of less than 10 µm is reached.

9. The process according to claim 8, wherein the grinding comprises a first coarse grinding followed by a fine grinding until 90% of the particles have a size of less than 6 µm.

10. The process according to claim 8 or 9, wherein the penetrant and the vegetable oil are mixed initially and the remaining ingredients of the mixture are added.

11. A method of controlling harmful insects, comprising applying the oil-suspension concentrate as defined in any one of claims 1 to 7, neat or diluted, to the insects or their habitat in an amount such that an effective amount of (A) and (B) acts on the insects or their habitat.

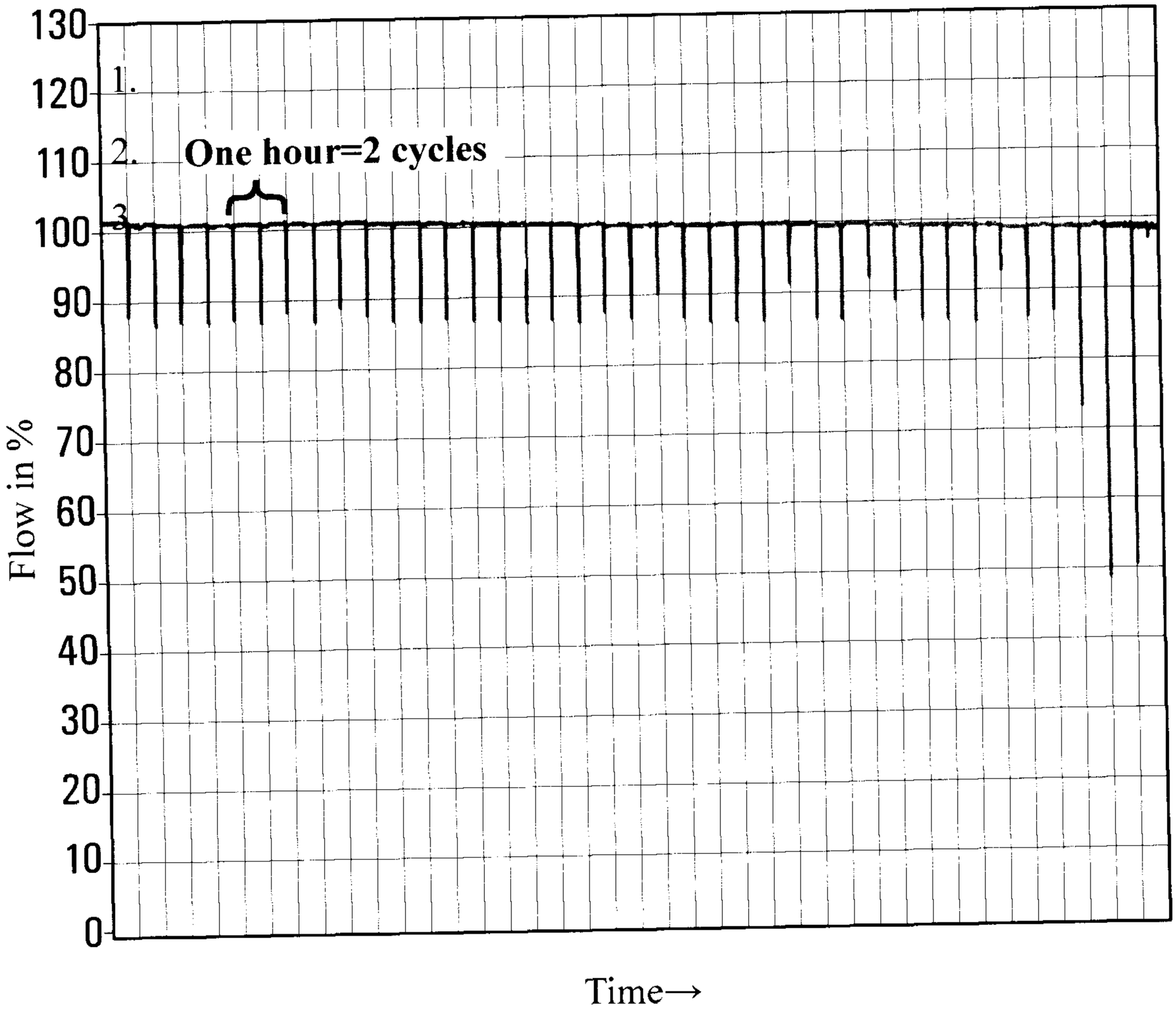
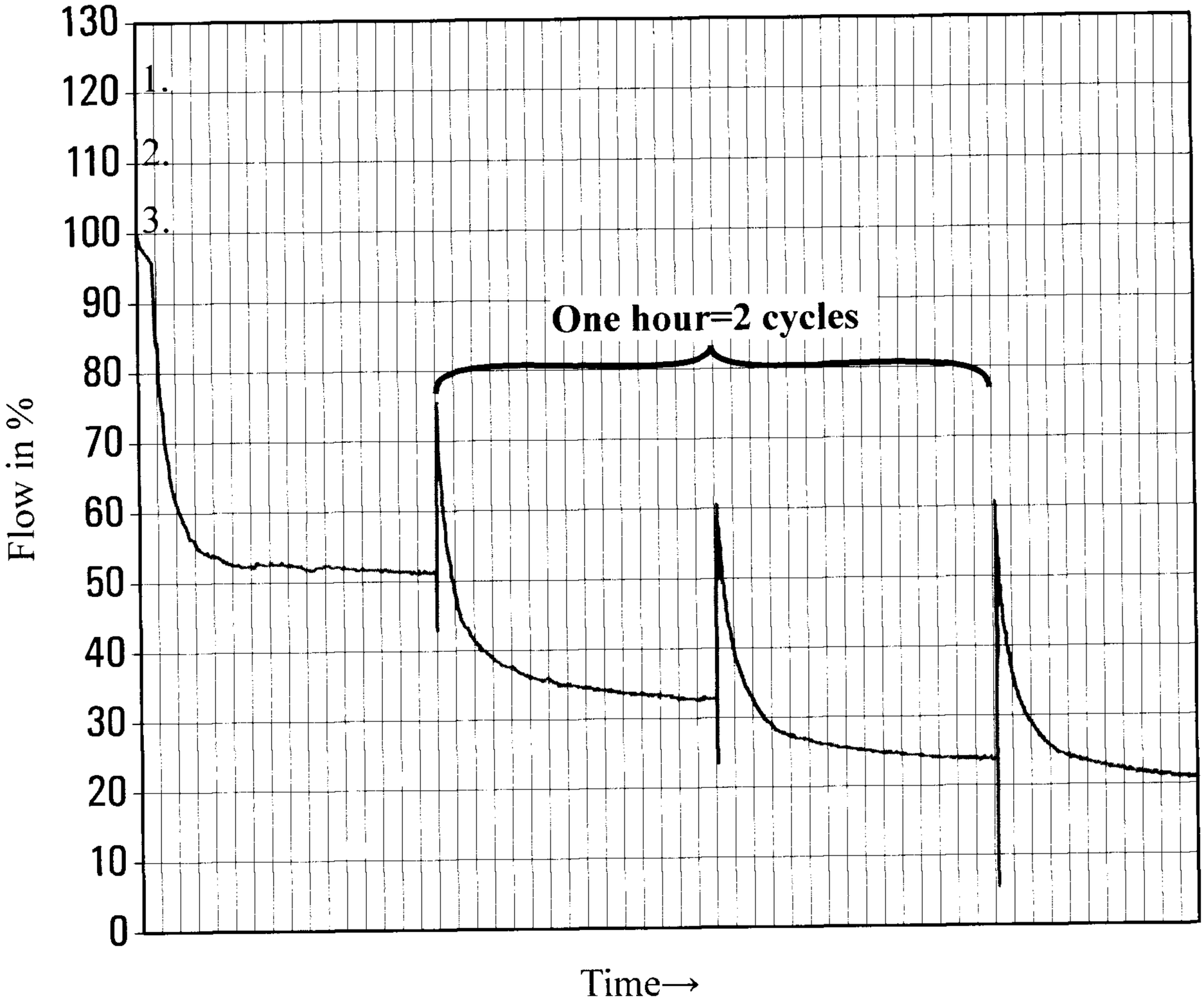

130
120
110
100
90
80
70
60
50
40
30
20
10
0
1.
2.
3
One hour=2 cycles
Flow in %
Time→

FIG. 1


130
120
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10
0
1.
2.
3.
One hour=2 cycles
Flow in %
Time→

FIG. 2

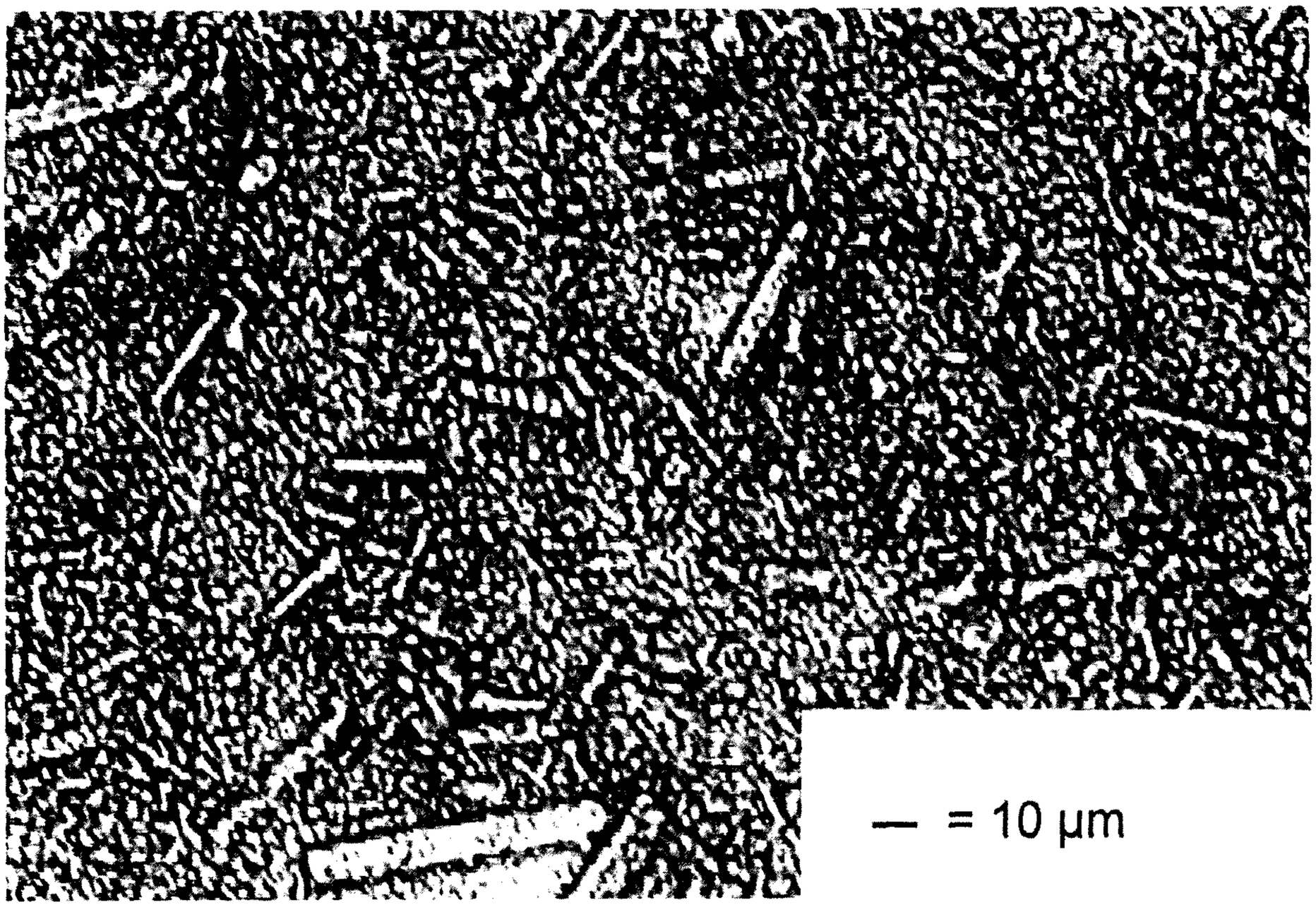

FIG. 3

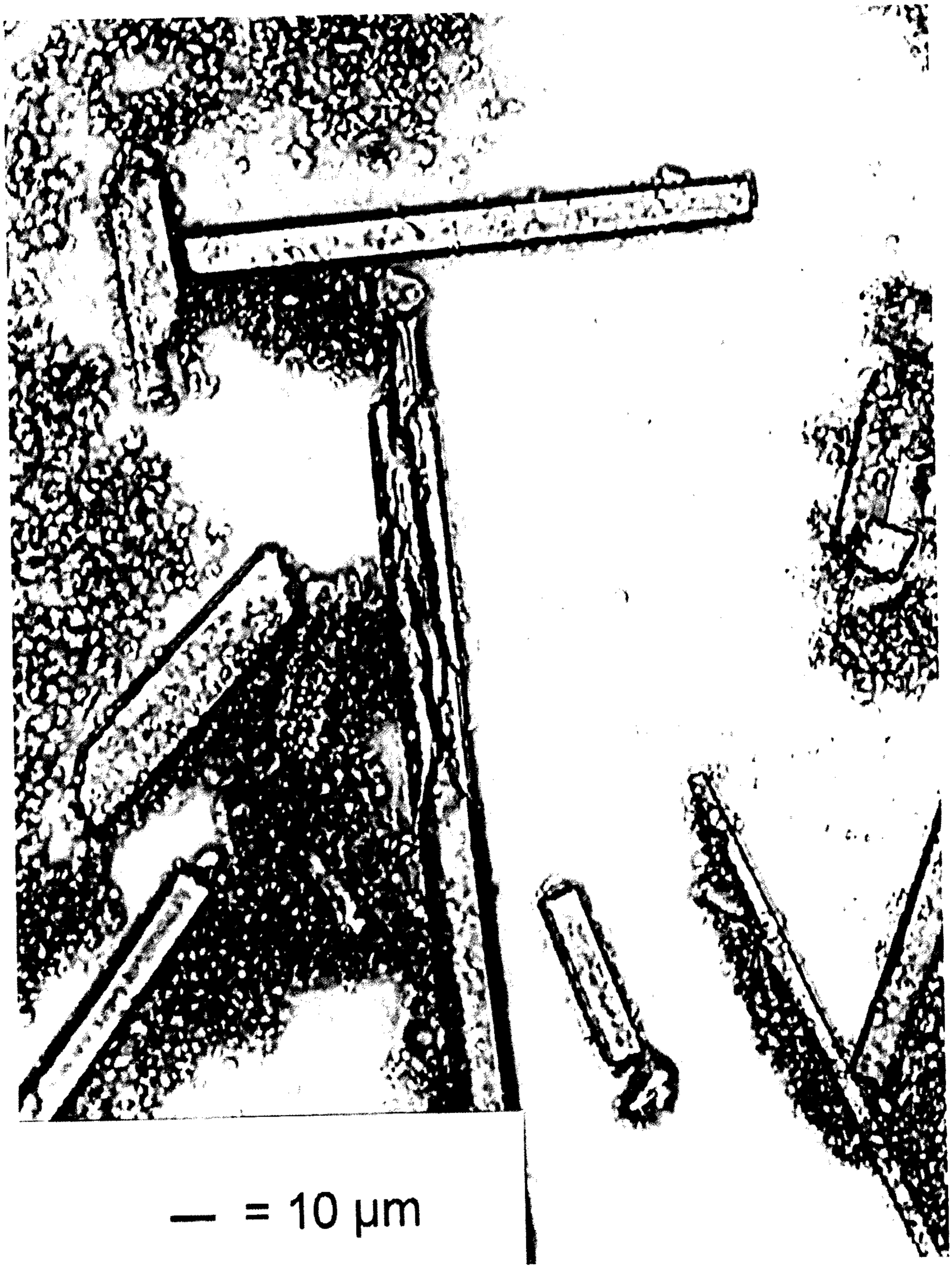

FIG. 4

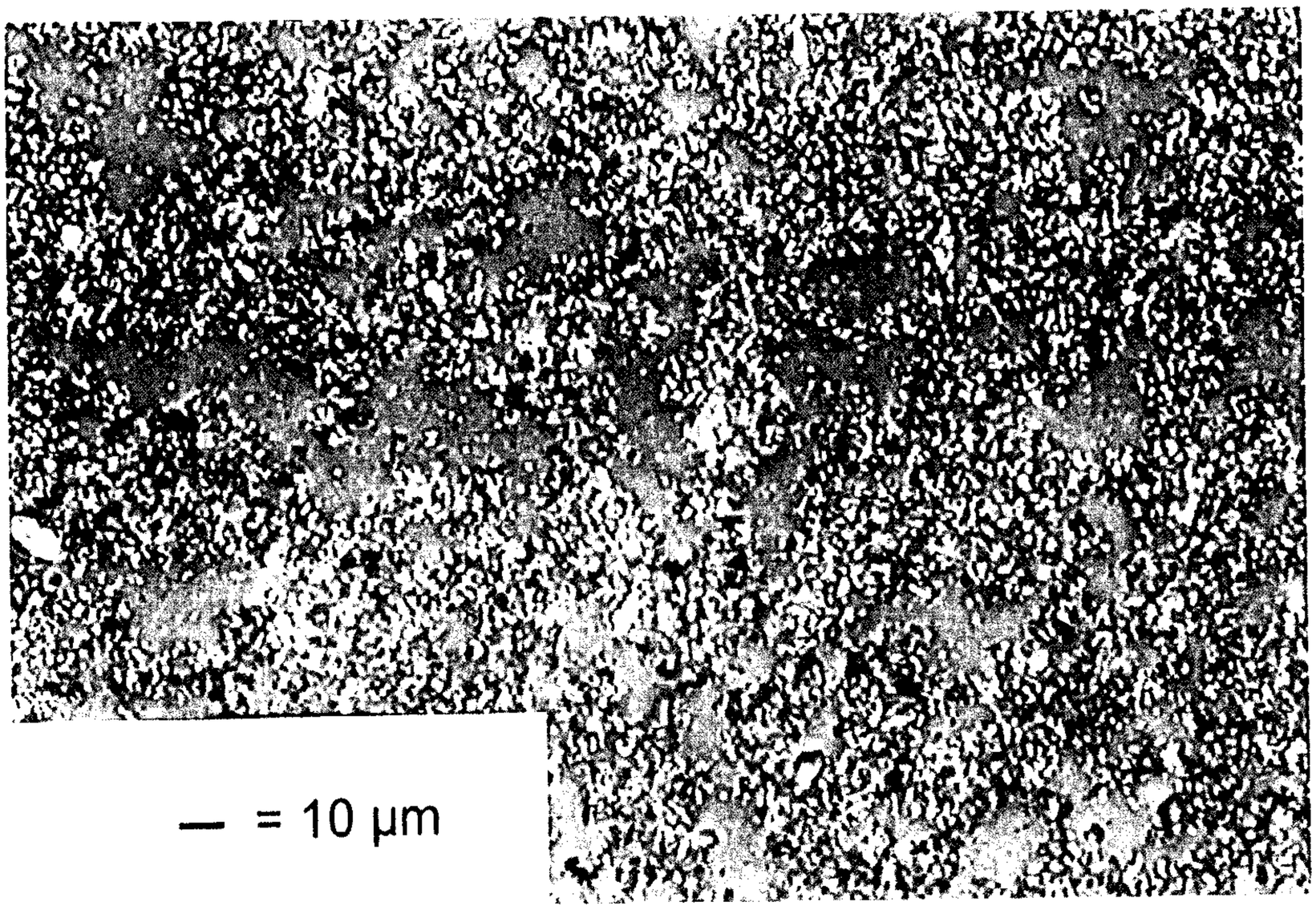

FIG. 5